

TITLE

FLUID CONDUIT AND PROCESS THEREFOR

FIELD OF THE INVENTION

5 The invention relates to a fluid conduit such as, for example, nozzle and a method for producing the conduit.

BACKGROUND OF THE INVENTION

If the surface of a conduit such as, for example, a nozzle, is adhered with materials such as a fluid or its dry form, the nozzle function can be hindered by
10 the materials adhered. One way to solve the problem is to wipe off the conduit to remove the adhering materials. It would be a great contribution to the art if the conduit can be made fluid-repellent. It would also be a great contribution to the art if the repellency is made abrasion-resistant and durable. It is also desirable to
15 freely select the thickness and site of application of a repellency layer generated on the nozzle, in accordance with the nozzle material, structure, dimension and usage.

The invention illustrates that a decline of a nozzle function can be avoided by applying a durable fluid-repellent layer to the nozzles so that the nozzle function cannot be hindered by the materials adhered. A fluid (such as ink) can be
20 ejected without high friction resistance or adhering to the nozzle. The invention also illustrates that repellency function can be obtained even if the layer is very thin (about 0.1-10000 nm). Therefore, the thickness of the layer does not influence the dimension of the conduit or device. For example, an ink jet printer nozzle has holes sized about 10-50 micrometer, such a thin layer does not impede
25 the nozzle's precise (accurate) function. If the layer thickness is thicker, the function of the nozzle can be greatly influenced.

SUMMARY OF THE INVENTION

A conduit having its surface applied or coated thereon with a thin layer in which the thin layer comprises, or is produced from, one or more fluorocarbon
30 silanes or hydrolyzates thereof.

DETAILED DESCRIPTION OF THE INVENTION

This application has a pending corresponding Japanese application 2002-337779, filed Nov. 21, 2002. The English translation of the Japanese application 2002-337779 is incorporated herein by reference. The term "conduit" refers to,
5 unless otherwise indicated, a device that transports or transfers a fluid. Examples of conduits include, but are not limited to, nozzles, tubes, pipes, cylinders, and combinations of two or more thereof. The term "nozzle" in this invention includes nozzles used not only in office machines such as printers, word processors, facsimiles, photocopiers, and the like, but also those used in
10 automobiles, molding machines, washing machines, printing machines, semiconductor-related machines, dispensers, and the like. One such nozzle is a plate nozzle having holes such as that used in a printer for ejecting ink. The word "surface" means not only an exterior surface, but also an interior surface of a conduit such as a nozzle. The term "fluid-repellency" represents the ability to
15 repel fluids over a broad range of fluids such as, for example, water, oils, emulsions, solid dispersions, liquid dispersions, pastes, adhesives, and the like.
20

A conduit can be made from any known substrate such as, for example, metal (such as stainless steel, aluminum, and the like), glass, ceramics, plastics, paper, tile, brick, concrete, wood, masonry, fiber, leather, stone, and combinations of two or more thereof.

The term "thin" refers to a thickness of less than about 0.1 to about 10,000, or less than about 1 to about 1,000 nanometers (nm).

The coating can be applied with any desired means of application such as dipping, brushing, spray vapor depositing, printing, spin coating, transferring,
25 flow coating and combinations of two or more thereof.

The fluorocarbon silane or its hydrolysate can be derived from an emulsion comprising the fluorocarbon silane or its hydrolyzate. The emulsion suitable can comprise a fluorocarbonsilane or its hydrolyzate, water, and optionally a surfactant, a silicone compound, or both and further optionally a catalyst. The emulsion can comprise a fluorocarbon silane or its hydrolyzate in the range of from about, 0.01 to about 40, preferably about 0.1 to about 20% by
30

weight. The molar ratio of the silicone compound moiety to the fluorocarbon silane or its hydrolyzate can be in the range of about 0.1:1 to about 10:1. The weight ratio of the fluorocarbon silane or its hydrolyzate to surfactant can be in the range of about 0.1:1 to about 10:1 or 1:1 to about 10:1. The catalyst can be
5 either an acid or a base. An effective amount of catalyst is generally the amount that can adjust the pH of the emulsion composition to 4.5 or less, such as about 2 to 4.5 or to 7 or more such as 7 to 12. Water generally makes up the rest of the emulsion.

The fluorocarbon silane can have the formula of $R_f-(CH_2)_p-Si(-(O-$
10 $CH_2CH_2)_n-OR^1)_3$ where R_f is at least one perfluoroalkyl group containing about 3 to about 18 carbon atoms; each R^1 can be the same or different alkyl groups containing 1 to about 3 carbon atoms; $p=2-4$; and $n=2-10$. R_f can also be a mixture of perfluoroalkyl groups containing an average of about 8 to about 12 carbon atoms; R^1 is methyl; and $p=2$; and $n=2-4$ (optionally $n=2-3$). When n is 2,
15 it can be a perfluoro alkyl ethyl tris(2-(2-methoxyethoxy)ethoxy)silane and when $n=3$, it can be perfluoro alkyl ethyl tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy) silane. Such fluorocarbon silanes can be prepared by any methods known to one skilled in the art.

Any silicon compound such as, for example, one comprising one or more
20 alkoxy groups or its partial condensation product can be used. For example, a silicate having the formula of $Si-(R)_4$ can be used in which R is one or more groups selected from the group consisting of OCH_3 , OCH_2CH_3 , and $(OCH_2CH_2)_mOCH_3$ ($m=1-10$). An organoalkoxysilane also can be used having the formula of $R^2_qSi(OR^3)_{4-q}$ in which each R^2 can be the same or different and is
25 independently an alkyl group containing about 1 to about 10 carbon atoms; each R^3 can be the same or different alkyl groups independently containing 1 to about 3 carbon atoms; and $q=1-3$. The alkyl group represented by R^2 can be substituted by, for example, amino, epoxy, vinyl, methacryoxy, thiol, urea, mercapto, or combinations of two or more thereof, and the like. Specific examples of
30 organoalkoxysilane compounds include, but are not limited to, dimethyldimethoxysilane, methyltrimethoxy silane, 3-aminopropyltriethoxy silane, N-(2-aminoethyl)3-aminopropylmethyldiethoxy silane, 3-

glycidoxypropyltrimethoxy silane, one or more partial condensation products thereof, and combinations of two or more thereof.

An acid or base can be used as catalyst. Such acid or alkaline substance can be any one known to one skilled in the art. For example, phosphoric acid, 5 boric acid, hydrochloric acid, sulfuric acid, nitric acid, acetic acid, formic acid, or combinations of two or more thereof, can be used. Similarly, ammonia, ammonium hydroxide, pyridine, sodium hydroxide, potassium hydroxide, or combinations of two or more thereof, can also be used.

Any surfactants that can stabilize the above-described emulsion may be 10 used. The surfactant generally is a surfactant having an HLB value sufficiently high to inhibit self-condensation of the fluorocarbon silane hydrolysis product. The term "HLB" refers to the HLB system published by ICI Americas Inc., Wilmington, Delaware; Adamson, A.W., "Physical Chemistry of Surfaces", 4th edition, John Wiley & Sons, New York, 1982). The surfactant can be anionic, 15 cationic, nonionic, amphoteric, or combinations thereof. The preferred surfactants are those with HLB values greater than 5, preferably greater than 12, and more preferably greater than 16. Examples of nonionic surfactants include, but are not limited to, R_f¹-CH₂CH₂-O-(CH₂CH₂O)₁₁-H, C₉H₁₉-C₆H₄-O-(CH₂CH₂O)₅₀-H, other nonionic surfactants, and combinations thereof. Examples of cationic 20 surfactants include, but are not limited to R_f¹-CH₂CH₂SCH₂CH(OH)CH₂N(CH₃)₃⁺Cl⁻, other cationic surfactants, and combinations thereof. Examples of anionic surfactants include, but are not limited to, C₁₂H₂₅(OCH₂CH₂)₄OSO₃⁻NH₄⁺, C₁₂H₂₇-C₆H₄-SO₃⁻Na⁺, other anionic surfactants, and combinations or two or more thereof. In each formula, R_f¹ is a 25 perfluoroalkyl group generally having about 3-18 carbon atoms. The preferred surfactants are nonionic surfactants having polyethylene glycol in the molecular chain. The use of a nonionic surfactant, such as R_f¹-CH₂CH₂-O-(CH₂CH₂O)₁₁-H wherein R_f¹ is a C₃₋₁₈ perfluoroalkyl group, is preferred.

A variety of additives, including inorganic and organic fillers, 30 antioxidants, heat stabilizers, ultraviolet absorbers, lubricants, waxes, colorants and crystallization promoters, either independently or combinations of a plurality thereof may be used.

The emulsion can be used as is or, if necessary, after dilution or other modification to the desired concentration, by application to the surface of a conduit using any means known to one skilled in the art. For example, impregnation, dipping, coating, spraying, or combinations of two or more thereof can be used. The emulsion-treated surface can be optionally heat-treated at about 5 150 to about 500°C, or 200 to 450°C for about 1 minute to about 10 hours. Heat treatment can accelerate hydrolysis of the fluorocarbon silane or hydrolysis of the alkoxy silane and copolycondensation of the hydrolyzate. A thin film containing a copolycondensate of a fluorocarbon silane, or its hydrolyzate, and an alkoxy silane 10 can be formed. The heat treatment temperature and time period can be set to the optimal values after taking into consideration such factors as the fluid repellency of the surface film and cost effectiveness of treatment.

The substrate surface can provide a highly adhering fluid-repellent layer regardless of whether the surface is pretreated or has a primer layer or not.

15 The following examples illustrate, but do not limit the scope of the invention, a nozzle having a fluid repellent layer and a method for formation thereof.

EXAMPLES

20 The components used were as follows.
A fluorocarbonsilane, which was a perfluoroalkyl mixture represented by Rf-(CH₂)₂-Si((O-CH₂CH₂)₂-OCH₃)₃, was used. R_f is F(CF₂)_k (k=6, 1-2wt%; k=8, 62-64 wt%; k=10, 23-30 wt%; k=12-18, 2-6 wt%).

25 A surfactant, a nonionic surfactant represented by R'_f-CH₂CH₂-O-(CH₂CH₂O)₁₁-H was used, where R'_f is a perfluoroalkyl group having 3-18 carbon atoms.

The silicate used was a tetrakis(2-(2-methoxyethoxy)ethoxy)silicate (Si(DEGM)₄). The organoaloxysilane was CH₃Si(OCH₃)₃.

Example 1

30 The surfactant at 30 parts by weight, relative to the fluorocarbon silane at 100 parts by weight, was dissolved in water and 10 weight % fluorocarbon silane was slowly added based on the total weight of the aqueous emulsion while stirring

by an ordinary stirring technique (magnetic bar). The self-condensation of the fluorocarbon silane was suppressed, and its hydrolyzed state was maintained. A phosphoric acid was added while measuring pH of the emulsion by a pH meter. When the pH reached 2.0, the addition of the phosphoric acid was stopped.

- 5 Organooalkoxysilane was added such that the molar fraction of the organooalkoxysilane with respect to the fluorocarbon silane was 0.45 to produce a water-based emulsion.

Then, after stirring for 2 to 4 hours, the emulsion was coated on a ceramic nozzle of substrate (dimension of a ceramic nozzle plate; 5mm x 25mm, thickness 10 0.5mm, pore size 40 micrometer), followed by baking for 60 minutes at 200°C in an oven. This resulted in a uniform (visual observation) formation of about 50 nm thick fluid-repellent layer on the substrate surface.

A measurement was made of the contact angle with respect to an oil-based ink (30% each of 2-butoxyethyl acetate, propanol, and cyclohexane) dropped on 15 the substrate surface according to conventional contact angle measurement method where the initial value was 63°, a high fluid-repellency.

In order to check the adhesion of the fluid-repellent layer to the substrate, the layer was subjected to an abrasion test using a rubber wiper (automotive type) to carry out 100 reciprocal repeated wiping motions on the layer. After the 100 20 reciprocal wipings, the layer exhibited an oil-based ink contact angle of 56°, substantially the same as the original 63°.

The nozzle thus prepared was mounted on an industrial inkjet printer to carry out an ink ejection test, which showed that good ejection continued with no ink adhering to the nozzle section. This nozzle was used for the ink ejection part 25 in an industrial inkjet printer.

Example 2

An aqueous emulsion, the same as that of Example 1, was coated onto a polyimide resin nozzle surface by dipping, followed by baking 60 minutes at 200°C in an oven. This resulted in a uniform formation of an about 50 nm thick 30 fluid repellent layer on the substrate surface.

Contact angles with respect to water and hexadecane were measured and high fluid-repellency was observed. It had a contact angle with respect to water

of 119° and a contact angle with respect to hexadecane of 77°. Water and hexadecane were used because the nozzle ejection components are both aqueous and oily so that these were used as the target of measurement for representative examples.

- 5 In order to confirm the adhesion of the fluid-repellent layer to the substrate, the fluid-repellent layer-treated nozzle was dipped in an organic solvent for an ultrasonic wave cleaning test.

- After an ultrasonic wave cleaning at 23°C for 150 minutes, the contact angle was 113°, with respect to water, and 75°, with respect to hexadecane.
- 10 Therefore, there was no drop in fluid-repellency after an ultrasonic wave cleaning, indicating a high durability.

Comparative Example 1

- A polyimide resin nozzle, the same as that of Example 2, was used without coating on which the contact angles on the surface with respect to water and hexadecane were measured. The contact angle with respect to water was 74° and with respect to hexadecane it was 8° showing insufficient fluid-repellency.

Example 3

- The surfactant at 30 parts by weight (relative to the fluorocarbon silane at 100 parts by weight) was dissolved in water and 10 weight % fluorocarbon silane was slowly added based on the total weight of the aqueous emulsion while stirring by an ordinary stirring technique (magnetic bar). The self-condensation of the fluorocarbon silane was suppressed, and its hydrolyzed state was maintained. Hydrochloric acid was added while measuring pH of the emulsion by a pH meter. When the pH reached 2.0, the addition of the phosphoric acid was stopped.
- 25 Tetrakis[2-(2-methoxyethoxy)ethoxy]silicate was added such that the molar fraction of the tetrakis[2-(2-methoxyethoxy)ethoxy]silicate was 0.45 to produce a water-based emulsion. Then, after stirring the emulsion for 2 to 4 hours, it was coated on the substrate.

A metal nozzle surface was coated with this emulsion, followed by baking for 60 minutes at 200°C. This resulted in a uniform formation of about 50nm thick fluid repellent layer on the substrate surface.

The layer was subjected to an abrasion test involving 100,000 reciprocal repeated abrasions using a silicone rubber blade, after which contact angles with respect to a dye ink and to water were measured. The specific sample conditions called for coating with the dye ink once and 10 wipes with the rubber blade.

The contact angle with respect to dye ink had an initial value of 87°, which was 67° after about 100,000 reciprocal abrasions. The contact angle with respect to water had an initial value of 118°, which was 91° after 100,000 reciprocal abrasions. Both evaluations reflected outstanding contact angles, showing good fluid-repellency and durability.

Comparative Example 2

A metal nozzle, the same as that of Example 3, was used for a measurement of the contact angle without any coating thereof, which turned out to be 36° with respect to water, confirming insufficient fluid-repellency.

Example 4

An aqueous emulsion the same as that of Example 3 was coated on a metal nozzle surface, followed by baking 60 minutes at 200°C. This resulted in a uniform formation of about 50nm thick fluid-repellent layer on the substrate surface.

The treated nozzle was used to eject a solvent (N-methylpyrrolidinone) for 15 days (8 hours/days), followed by a frequent wiping with cloth and with silicone rubber, after which contact angles with respect to xylene and toluene were measured.

The initial value for the contact angle with respect to xylene was 70°, while that with respect to toluene was 68°. After wiping, the contact angles with respect to xylene and toluene were held at 70° or higher, confirming excellent fluid repellency and durability.

Comparative Example 3

A metal nozzle, the same as that of Example 4, was used without being coated with the emulsion, on which contact angles with respect to xylene and toluene were measured with no surface coating to give a contact angle with
5 respect to xylene of 4° and that with respect to toluene of 7°, confirming insufficient-fluid repellency.

In these examples, nonionic surfactants were used as a surface surfactant component, but any type can be used as long as it can stabilize the emulsion, including anionic, cationic, nonionic, amphoteric, or any other known surfactant
10 types. The silicon compound can be any type which can be added to increase the adhesion of the film.